Effect of TCE Concentration and Dissolved Groundwater Solutes on NZVI-Promoted TCE Dechlorination and H₂ Evolution

Y U E Q I A N G   L I U , [†]
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Nanoscale zero-valent iron (NZVI) is used to remediate contaminated groundwater plumes and contaminant source zones. The target contaminant concentration and groundwater solutes (NO_3^-, Cl^-, HCO_3^-, SO_4^{2-}, and HPO_4^{2-}) should affect the NZVI longevity and reactivity with target contaminants, but these effects are not well understood. This study evaluates the effect of trichloroethylene (TCE) concentration and common dissolved groundwater solutes on the rates of NZVI-promoted TCE dechlorination and H₂ evolution in batch reactors. Both model systems and real groundwater are evaluated. The TCE reaction rate constant was unaffected by TCE concentration for [TCE] ≤0.46 mM and decreased by less than a factor of 2 for further increases in TCE concentration up to water saturation (8.4 mM). For [TCE] ≥ 0.46 mM, acetylene formation increased, and the total amount of H₂ evolved at the end of the particle reactive lifetime decreased with increasing [TCE], indicating a higher Fe^0 utilization efficiency for TCE dechlorination. Common groundwater anions (5mN) had a minor effect on H₂ evolution but inhibited TCE reduction up to 7-fold in increasing order of Cl^- < SO_4^{2-} < HCO_3^- < HPO_4^2. This order is consistent with their affinity to form complexes with iron oxide. Nitrate, a NZVI-reducible groundwater solute, present at 0.2 and 1 mN did not affect the rate of TCE reduction but increased acetylene production and decreased H₂ evolution. NO_3^- present at >3 mM slowed TCE dechlorination due to surface passivation. NO_3^- present at 5 mM stopped TCE dechlorination and H₂ evolution after 3 days. Dissolved solutes accounted for the observed decrease of NZVI reactivity for TCE dechlorination in natural groundwater when the total organic content was small (<1 mg/L).

Introduction

Nanoscale zero-valent iron (NZVI) degrades many refractory contaminants in groundwater and soil (*1−6*). NZVI is highly reactive because of its high specific surface area and can be made to be mobile through water-saturated aquifer materials for in situ applications (*7*). Pilot tests have demonstrated the feasibility of delivering NZVI in situ (*8−10*), and it is promising for field application because of its potentially stable long-

term reactivity and slow Fe^0 decay rates at pH >7.5 (*11*). Most NZVI reactivity studies use low contaminant concentrations in clean systems (e.g., DI water), however, contaminant concentration, competing reactive solutes such as NO_3^-, and common dissolved groundwater solutes may affect the reactivity and lifetime of NZVI. The effects of contaminant concentration and groundwater solutes on NZVI reactivity are not well understood but are needed to predict the reactivity, longevity, and efficacy of NZVI treatment under realistic in situ conditions to ensure efficient field application.

NZVI has been used to treat chlorinated solvent contaminant plumes (*10*), where the contaminant concentration is typically low (micromolar or less) and chlorinated solvent dense nonaqueous phase liquid (DNAPL) contaminant source zones (*12*), where the contaminant concentration is high (millimolar) and may be near saturation (e.g., 8.4 mM for TCE) at the DNAPL−water interface. TCE concentration may affect the TCE reaction rate, distribution of reaction intermediates and products, and H₂ evolution from NZVI. For micron-sized iron filings, the TCE reaction rate constant decreased with increasing TCE concentration (up to 7.8 mM in a column study (*13*) and 0.3 mM in a batch study (*14*)) because of reactive site saturation and increased iron passivation. In contrast, the dechlorination rate of chlorinated ethanes was independent of their concentration for NZVI made from the reduction of dissolved iron by sodium borohydride (*1*). The effect of TCE concentration on the reactivity of reactive nanoscale iron particles (RNIP) that have physical and chemical properties more like iron filings (*2, 3*) has not been reported. The TCE concentration may also affect H₂ evolution. With RNIP, H₂ evolution was higher in the absence of TCE than in the presence of TCE, presumably because of competition between TCE and H^+ for reactive sites (*3*). A higher TCE concentration should therefore decrease the rate and extent of H₂ evolution from RNIP. Increasing the TCE concentration may also yield a lower TCE reaction rate or reaction order (*4, 15*) and alter the distribution of TCE reaction intermediates and products (*3*).

NZVI reactivity may also be influenced by inorganic anions in groundwater including Cl^-, SO_4^{2-}, HCO_3^-, and NO_3^-. The latter two are particularly important because of their potential negative effects on NZVI longevity and reactivity (*16, 17*). While typically low in pristine groundwater, phosphate species (HPO_4^{2-}) may be present in a contaminated aquifer because they are sometimes used to enhance bioremediation (*18*). Appreciable changes in the reactivity of iron filings have been observed with these groundwater solutes present (*13, 19−22*). Potential mechanisms for solute effects on the reactivity of iron filings include (1) competition for reactive cathodic sites by Fe^0-reducible solutes (e.g., NO_3^- (*13, 23*)), (2) formation of a passivating oxide layer which blocks access to reactive sites (e.g., HCO_3^-, SO_4^{2-}, HPO_4^{2-} (*16, 19, 21, 24*)), or (3) dissolution of the iron oxide layer leading to increased reactivity (e.g., Cl^-, HCO_3^-, SO_4^{2-} (*19, 21, 24*)). The effects of these groundwater solutes on NZVI reactivity have not been reported and are needed to interpret TCE reactivity data from field applications where these solutes are present.

Most reported NZVI studies have used low TCE concentrations without dissolved groundwater solutes. The objective of this study was to assess the effect of TCE concentration and major groundwater anions on the NZVI-promoted reduction of TCE and H^+ (to form H₂). Specific objectives were (1) to quantify the effect of increasing the TCE concentration to near saturation on H₂ evolution, the rate of TCE reduction, and the TCE reaction products formed, (2) to determine the effect of Fe^0-reducible (NO_3^-) and Fe^0-

unreducible (Cl^-, SO_4^{2-}, HCO_3^-, and HPO_4^{2-}) dissolved groundwater solutes on H_2 evolution, the rate of TCE reduction, and the TCE reaction products formed, and (3) to explain the effect of groundwater solutes on the NZVI-promoted reduction of TCE in real groundwater. TCE disappearance, reaction products, and H_2 evolution were measured in batch reactors at initial TCE concentrations ranging from 0.027 mM (3.5 mg/L) to saturation (8.4 mM or 1100 mg/L) and in the presence of (5 mN) groundwater solutes including Cl^-, SO_4^{2-}, HCO_3^-, $H_2PO_4^-$, and NO_3^-. TCE dechlorination in real groundwater (2 sites) and in a synthetic groundwater was measured to determine if the lower observed reactivity in real groundwater can be attributed solely to the presence of dissolved solutes.

Materials and Methods

Chemicals. TCE (99.5+%), *cis*-1,2-dichloroethylene (c-DCE) (98%), *trans*-1,2-dichloroethylene (t-DCE) (98%), and 1,1-dichloroethylene(1,1-DCE) (99%) were from Aldrich. Methanol (histological grade) was from Acros. Chloride (99%), bicarbonate (99%), sulfate (99%), nitrate (99%), and phosphate (99%) were from Fisher Scientific. Olefin standards (1000 ppm of ethylene, propene, butene, pentene, and hexene), paraffin standards (1020 ppm of methane, ethane, propane, butane, pentane, and hexane), acetylene (1000 ppm and 1%), ethylene (1%), ethane (1%), vinyl chloride (VC) (10 ppm), and hydrogen (1.08%) were from Alltech. The balance of each gas standard was N_2, and all reported concentrations are ±2% of the reported concentration. Ultrahigh-purity argon, hydrogen (5.18%), and N_2 were from Butler Gas products (Pittsburgh, PA).

RNIP and Groundwater. RNIP was supplied by Toda Kogyo Corp. (Onoda, Japan). To preserve the Fe^0 in the particles, RNIP was dried as previously described (*11*) and stored in an anaerobic glovebox prior to use. The Fe^0 content of the particles (48 wt %) was determined by acid digestion and measurement of the H_2 formed, as previously described (*4*). The remaining 52 wt % is assumed to be Fe_3O_4. Groundwater samples were collected from a TCE-contaminated site in Parris Island, SC (SC-GW), and in Mancelona, MI (MI-GW). Groundwater was stored at 4 °C and deoxygenated by N_2 sparging prior to use. Solution pH was measured after N_2 sparging. Dissolved anions and cations were determined by a commercial laboratory (Severn Trent Laboratories, Pittsburgh, PA) for the Parris Island groundwater and provided by the Michigan Department of Environmental Quality Environmental Laboratory (Lansing, MI) for the Mancelona site groundwater. Total organic carbon (TOC) was measured using UV/persulfate wet oxidation (OI Analytical Model 1100). Synthetic groundwater (SC-SGW and MI-SGW) was prepared with calcium, sodium, or potassium salts of each anion to approximate the major anion and cation composition of the groundwater (Supporting Information Table SI-1) but without organic carbon.

Batch Experiments. All reactors were 70 mL serum bottles containing 30 mL of solution and 40 mL of headspace. Two sets of experiments were prepared. The first set evaluated the effect of TCE concentration on NZVI reactivity in HEPES buffer at pH 7. The second set evaluated the effect of dissolved ions at pH 8.9, which is the equilibrium pH of the zerovalent iron and water system (*11*) without added buffer. The preparation of each is described.

Effect of TCE Concentration. In a preliminary study, a high TCE concentration (1.5 mM) reacting with NZVI generated H^+ and Cl^- and decreased the reactor pH to <5. Thus buffer was necessary to control the pH in these reactors. Each reactor contained 670 mg/L of RNIP (48 wt % Fe^0) in 50 mM HEPES ($pK_a = 7.5$) buffer. The initial pH was adjusted to 7.0 by addition of NaOH solution. The 50 mM HEPES buffer provided good buffer capacity at pH 7 and has been

TABLE 1. TCE Reaction Rate Constant under Various TCE and Solutes Conditions

solutes	initial[TCE]$_{aq}$ (mM)	buffer	initial pH	final pH	k_{TCE} ($\times 10^3$ L h^{-1} m^{-2})^a
TCE only	0.027	none	8.9	9.5	5.4 ± 0.23
TCE only	0.027	50 mM HEPES	7.0	7.4	1.1 ± 0.1
TCE only	0.11	50 mM HEPES	7.0	7.4	1.2 ± 0.1
TCE only	0.46	50 mM HEPES	7.0	7.2	1.2 ± 0.1
TCE only	1.3	50 mM HEPES	7.0	7.1	0.64 ± 0.07
TCE only	8.4	50 mM HEPES	7.0	6.9	0.78 ± 0.09
NO_3^-(0.2 mM)	0.027	none	8.9	9.9	7.5 ± 0.2
NO_3^-(1 mM)	0.027	none	8.9	10.4	6.7 ± 0.2
NO_3^-(3 mM)	0.027	none	8.9	10.6	1.9 ± 0.1
NO_3^-(5 mM)	0.027	none	8.9	10.6	0.9 ± 0.03
Cl^-	0.027	none	8.9	9.5	3.8 ± 0.2
SO_4^{2-}	0.027	none	8.9	9.7	2.0 ± 0.15
HCO_3^-	0.027	none	8.9	9.9	1.6 ± 0.07
HPO_4^{2-}	0.027	none	8.9	10.2	0.76 ± 0.03
SC-GW	0.027	none	5.6	8.8	0.73 ± 0.02
SC-SGW	0.027	none	6.0	9.2	1.6 ± 0.2
MI-GW	0.027	none	6.0	9.3	1.55 ± 0.11
MI-SGW	0.027	none	6.0	9.5	1.74 ± 0.15

^{a} All reported rate constants are duplicates except those at different initial TCE concentration. Rate constants and confidence intervals are determined from fits of both sets of experimental data.

used in previous studies with Fe^0 and FeS (*1, 11, 25, 26*). Aliquots of 0.15 and 0.6 mL of saturated TCE solution were added to each reactor to provide initial TCE concentrations of 0.027 and 0.11 mM, while 1.8, 5.4, or 45 μL of pure-phase TCE was added to provide an initial concentration of 0.46, 1.3 mM, or saturated TCE (8.4 mM, with ~11 μL remaining pure-phase TCE), respectively.

Effect of Dissolved Solutes. Experiments evaluating the effect of dissolved solutes were conducted without buffer by addition of 5 mN individual solutes (i.e., 5 mM Cl^-, HCO_3^-, and NO_3^-; 2.5 mM SO_4^{2-} and HPO_4^{2-}) to DI water as their respective Na^+ salt. Since the equilibrium pH of a 2 g/L RNIP solution was 8.9, the initial solution pH was adjusted to 8.9 by addition of 10 mM NaOH. Each reactor contained 2 g/L RNIP ([Fe^0] = ~17 mM) and was spiked with 0.15 mL of saturated TCE solution to provide an initial TCE concentration of 0.027 mM. Reactors to measure TCE reduction in groundwater and synthetic groundwater were prepared identically. Solution pH was measured in an anaerobic glovebox at the end of each experiment.

Analytical Methods. A 100 μL headspace sample was withdrawn from reactors and analyzed for TCE and its products using a 30 m GSQ PLOT capillary column on a HP 6890 GC/FID or H_2 using GC/TCD as described in (*4*). TCE reduction by RNIP was assumed to follow previously published reaction pathways (*3*), but it was assumed here that all TCE reduction occurred via β-elimination to form acetylene, followed by acetylene reduction to ethene and ethane (Scheme SI-1, Supporting Information). This modification was made on the basis of the observation of a constant ratio of ethene to ethane formed in each reaction, while TCE was present, suggesting that their production was concomitant. The reaction rate constant (k_{TCE}) was evaluated using a kinetic modeling software package, Scientist, version 2.01 (Micromath, St. Louis, MO), by fitting the loss of TCE and formation of products (acetylene, ethene, and ethane) concurrently. The reported reaction rate constants (Table 1), k_{TCE}, are those that would be observed in water without headspace because this best represents application in a
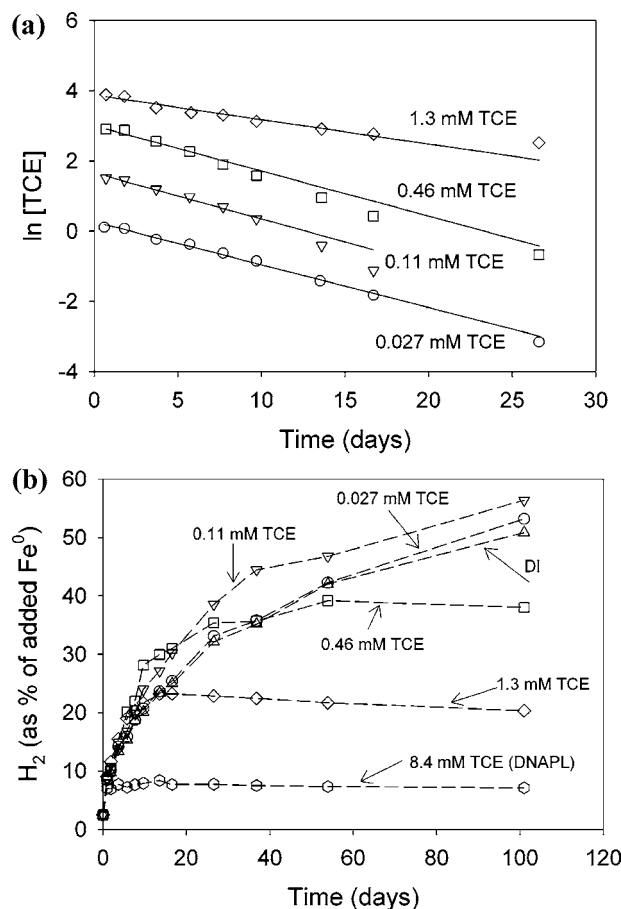
(a)

(b)

FIGURE 1. Effect of TCE concentration on the TCE dechlorination and H$_2$ evolution rate using 670 mg/L RNIP (48 wt% Fe^0), pH 7.0, buffered with 50 mM HEPES. (a) TCE (in μmol) reduction. Lines are the pseudo-first-order fits of the data. (b) H$_2$ evolution (as wt%Fe^0 in particles) assuming 2.67 electron equivalents per mole of Fe^0.

saturated groundwater aquifer (eq SI-1, Supporting Information).

Results and Discussion

Effect of TCE Concentration. TCE loss by NZVI at different initial TCE concentrations is shown in Figure 1a. The corresponding rate constants (k_{TCE}) are provided in Table 1. Good data fits were achieved using pseudo-first-order reaction kinetics for concentrations from 0.027 to 0.46 mM. TCE loss at an initial TCE concentration of 1.3 mM had an acceptable pseudo-first-order fit (Figure SI-1d), but the slowing reaction at later times suggests a decrease in reactivity with time that was not observed at lower initial TCE concentrations. When the minor effect of deactivation is ignored, a less than 2-fold decrease of k_{TCE} over a TCE concentration range from 0.027 to 1.3 mM was observed (Table 1). This is consistent with previously reported observations with a different type of NZVI, where the observed reaction rate constant for pentachloroethane (PCA) was nearly constant over a PCA concentration range of 0.025−0.125 mM in unbuffered systems (1). A similar ~2-fold decrease in reactivity at higher TCE concentrations was reported by Farrell et al. (2000) for ZVI filings and was attributed to deactivation caused by formation of a passivating Fe-oxide layer.

In the presence of TCE DNAPL, the headspace TCE concentration does not change so k_{TCE} (Table 1, [TCE] = 8.4 mM) was determined on the basis of the initial acetylene formation ($t \leq 2$ d) according to eq 1

$$k_{TCE} = \frac{a_{ACY}}{C_{TCE,S}V_wC_{Fe,SA}} \quad (1)$$

where a_{ACY} is the initial acetylene (mass) formation rate (Supporting information Figure SI-1e), $C_{TCE,S}$ is TCE saturation concentration (8.4 mM), V_w is the water solution volume, and $C_{Fe,SA}$ is the iron surface concentration (20 m^2/L). The derivation of eq 1 and the validity of its application are provided in Supporting Information. The calculated k_{TCE} in the presence of TCE DNAPL was similar to that observed for a 1.3 mM initial TCE concentration (Table 1). While the initial rate ($t \leq 2$ days) is rapid, the deviation from the expected zero-order kinetics of acetylene formation at later times indicates that the TCE dechlorination rate is slowing near the end of the particle's reactive lifetime, which was 10 d with TCE DNAPL present as described below. Some deactivation at high TCE concentration (1.3 and 8.4 mM) is consistent with previous reports where a deactivation rate constant was needed to adequately fit TCE loss at higher TCE concentration (1.8 mM aqueous TCE) for RNIP (3). Overall, the effect of TCE concentration on k_{TCE} at pH 7 (in HEPES buffer) was small, that is, k_{TCE} was independent of TCE concentration up to at least 0.46 mM, and changed by less than a factor of 2 for further increases in TCE concentration up to water saturation (8.4 mM).

The *rate* of H$_2$ evolution in HEPES buffer at pH 7.0 (final pH 7.4) was unaffected by the presence of TCE compared to that in the absence of TCE; however, the TCE concentration did affect the total amount of H$_2$ that was evolved at the end of the particle's reactive lifetime (Figure 1b). H$_2$ evolution stopped after 6, 18, and 54 d at initial TCE concentrations of 8.4, 1.3, and 0.46 mM, respectively, when H$_2$ accounted for 7, 23, and 40% of the Fe^0 in the particles, respectively (assuming that Fe^0 is oxidized to Fe$_3$O$_4$ and provides 2.67 electron equivalents per mole of Fe^0 (11)). TCE and H$^+$ are competing oxidants for Fe^0, and evolved H$_2$ cannot be used by RNIP for TCE reduction (3). The reduction in total evolved H$_2$ with increasing TCE concentration therefore indicates that TCE is outcompeting H$^+$ as an oxidant as the TCE concentration increases at a fixed [H$^+$] (pH). The absence of an effect of TCE on the *rate* of H$_2$ evolution, however, suggests that TCE and H$^+$ are not competing for the same reactive sites.

The TCE concentration also affected the particle reactive lifetime. At an initial [TCE] $\leq$ 0.11 mM, TCE was completely degraded without using all of the available Fe^0 in the particles, and thus, H$_2$ evolution continued throughout the experiment. For [TCE] $\geq$ 0.46 mM, all of the available Fe^0 was consumed, and H$_2$ evolution ceased (Figure 1b). The particle reactive lifetime was estimated to be ~10, ~40, and ~60 d at TCE concentrations of 8.4, 1.3, and 0.46 mM, respectively, because thereafter no additional TCE reaction products were formed, and TCE and acetylene persisted in the reactors. The decreasing portion of Fe^0 used to reduce water to form H$_2$ at increasing TCE concentration indicates that NZVI use in source areas with high TCE concentrations can potentially increase the Fe^0 utilization efficiency for TCE reduction but also results in more rapid consumption of Fe^0 and a shorter reactive lifetime.

In addition to the decreased H$_2$ evolution, a higher initial [TCE] increased the yield of acetylene. For initial aqueous [TCE] $\leq$ 0.46 mM, the ratio of acetylene formed to ethene and ethane formed is independent of the initial TCE concentration (Supporting Information Figure SI-1a−c). However, at [TCE] $\geq$ 1.3 mM, there is an increase in acetylene formation relative to ethene and ethane, and in the presence of DNAPL, acetylene accounted for 86% of the products (10% was ethene and 4% was ethane) when the reaction stopped (Supporting Information Figure SI-1d−e). The increase in
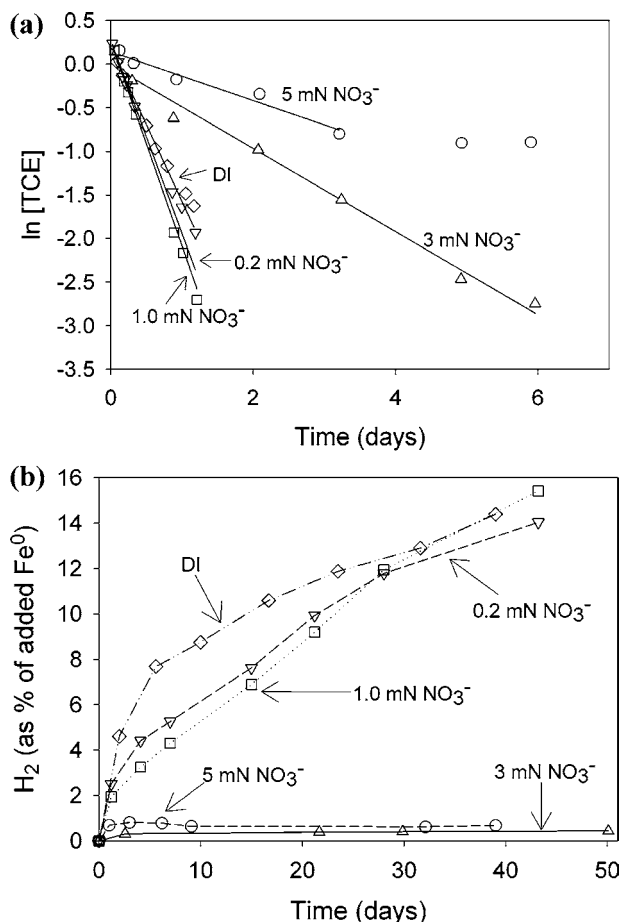
(a)

(b)

FIGURE 2. Effect of the competing solute NO_3^- (0, 0.2, 1.0, 3.0, 5.0 mN) on the TCE dechlorination and H_2 evolution rate using 2 g/L RNIP (48 wt% Fe^0) at pH 8.9 (unbuffered), $[TCE]_0 = 0.027$ mM. (a) Effect on TCE (in μmol) reduction. Lines are the pseudo-first-order fit of the data. (b) H_2 evolution (as wt%Fe^0 in particles) assuming 2.67 electron equivalents per mole of Fe^0. Lines are not a fit of data and are used only to guide the eye.

acetylene yield could be the result of TCE outcompeting acetylene for reactive sites or because there is a limited amount of adsorbed H on the NZVI surface at high oxidant loadings, which favors the formation of less-reduced reaction intermediates and products.

Effect of Nitrate. Nitrate, a Fe^0-reducible groundwater solute, affected H_2 evolution and TCE reduction by NZVI (Figure 2a−b). An initial $[NO_3^-] \leq 1$ mN slightly enhanced TCE reaction rates compared to DI water (Table 1), but initial $[NO_3^-] \geq 3$ mN inhibited TCE reduction. The degree of inhibition increased with increasing nitrate concentration (a 3-fold decrease at 3 mN NO_3^- and a 7-fold decrease at 5mN NO_3^- compared to DI water). With 5 mN initial $[NO_3^-]$, only 60% of the TCE added to the reactor was transformed at the end of the RNIP reactive lifetime, whereas $\geq$99% of the TCE was transformed in reactors with 3 mN NO_3^- or less. The solution pH measured after reaction in reactors initially containing nitrate was 0.5−1 pH unit higher than without nitrate because of NO_3^- reduction (26). Nitrate reduction was confirmed in this study by measurement of the nitrate concentration at the end of this ∼100-day experiment (0.85 mM) for an initial NO_3^- concentration of 5 mM. Nitrate reduction to nitrite and ammonia by NZVI was previously reported (27), but these products were not measured here.

Inhibition of TCE reduction in the presence of nitrate is not unexpected because inhibition of TCE reduction by iron filings caused by NO_3^- is documented (13, 23), and potentiometry measurements during carbon steel corrosion have indicated that NO_3^- passivates the surface because of the formation of FeOOH (28). One possible explanation for the observed inhibition at $[NO_3^-] \geq 3$ mM is competition between NO_3^- and TCE for reactive sites. In this case, the absence of inhibition of the TCE reaction ($C_{TCE} = 0.027$ mM) in the presence of up to 1 mN NO_3^- indicates low NO_3^- surface coverage at the lower $[NO_3^-]$, consistent with the expectation of a low affinity of NO_3^- for the negatively charged NZVI surface (29). At the higher $[NO_3^-]$, the NO_3^- surface coverage increases to a point where it competes with TCE for reactive sites, resulting in inhibition of TCE dechlorination. However, a more likely explanation is that the inhibition is caused by surface passivation at the high nitrate concentration, which shifts the TCE reduction reaction from cathodic control (i.e., reduction of TCE) to anodic control (i.e., release of Fe^{2+} and electrons) (13). Fe^0 was detected in RNIP recovered from the 5 mN NO_3^- reactor, even though TCE was no longer degrading, indicating that the NZVI surface had been passivated. It should be noted that an elevated pH of 10 (∼1 pH unit compared to the DI water case) can inhibit the reaction because of the formation of a passivating iron oxide layer (e.g., FeOOH or a nonporous maghemite) (23, 30, 31). However, inhibition was not observed at 1 mN NO_3^- at a similar pH, so NO_3^--promoted surface passivation at high NO_3^- concentration is the most likely explanation for inhibition of the TCE dechlorination reaction (23). Regardless of the mechanism, the effect of NO_3^- is only apparent at a $[NO_3^-] > 1$ mM, which is much greater than would be expected in contaminated groundwater.

H_2 evolution was relatively unaffected by the presence of $NO_3^- \leq 1$ mN. At early times, where NO_3^- is being reduced by NZVI (the $[NO_3^-]$ was below detection limit after 22 days for initial nitrate concentrations less than 1 mM), H_2 evolution was slightly inhibited relative to DI water. Similar to the cases at high initial [TCE], NO_3^- initially at 3 or 5 mN is outcompeting H^+ for Fe^0 because of its high concentration relative to H^+ under anodic control when the surface was passivated, thereby inhibiting H_2 evolution. Further, the electron equivalents required to convert 4.15 mM NO_3^-, lost from solution for the case with an initial NO_3^- concentration of 5 mM to NH_4^+ is 33.2 mM, which accounts for ∼70% of the electron equivalents added to the reactors (as Fe^0). This suggests that much of the available Fe^0 was used to reduce NO_3^- and is consistent with Farrell et al. and Schlicker et al., who both found that the rate of nitrate reduction was faster than TCE reduction (13, 23). The presence of NO_3^- also increased the acetylene yield relative to reactors without NO_3^-. This shift to less-reduced reaction intermediates and products is consistent with the decrease in H_2 evolution, that is, less adsorbed H on the particle surface because of scavenging by NO_3^-.

Effect of Noncompeting Dissolved Groundwater Solutes. The anions Cl^-, SO_4^{2-}, HCO_3^-, and HPO_4^{2-} are assumed to be inert with respect to reduction by Fe^0 and thus do not compete for electrons and atomic H. TCE reduction in the presence of individual dissolved solutes remained pseudo-first-order with respect to TCE (Figure 3a and b); however, the presence of any anion (5 mN) decreased NZVI reactivity with TCE in increasing order $Cl^- < SO_4^{2-} < HCO_3^- < HPO_4^{2-}$ (Figure 3a). Inhibition of TCE reduction by phosphate (as hydrogen phosphate, $HPO_4^{2-}_{(aq)}$) was 7-fold compared to that in DI water (Table 1). The order of the effect is consistent with the affinity of anion complexation to hydrous ferric oxide (HFO) $Cl^- < SO_4^{2-} < HCO_3^- < HPO_4^{2-}$ at pH 8.9, based on their reported stability constants (32−34), suggesting that the inhibitory effect of these solutes on TCE reduction may be attributed to passivation of reactive sites from Fe−anion complexes formed on the iron surface. The same order for the effect of dissolved anions on the reduction of NO_3^- by iron filings was reported by Su and Puls (16). The greater
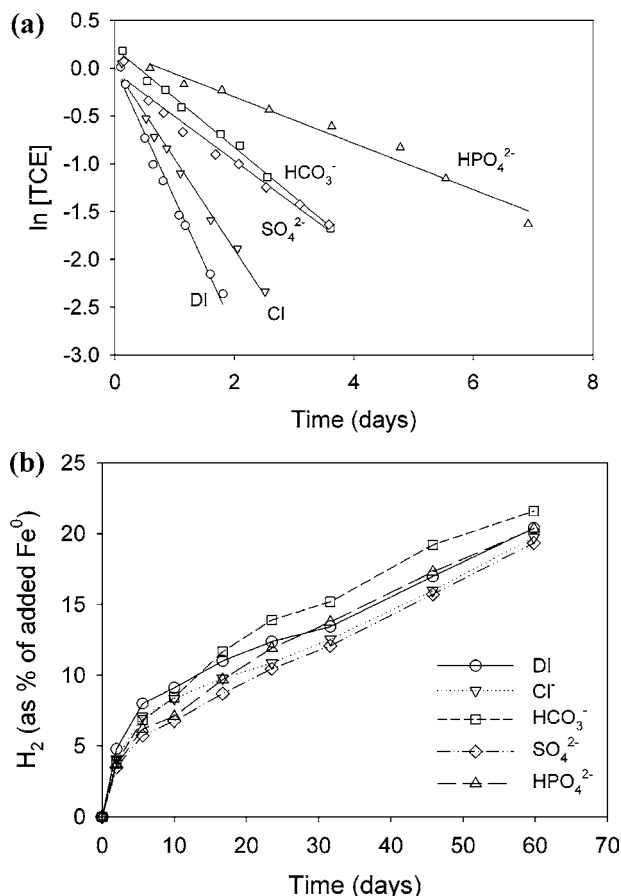
(a)

(b)

FIGURE 3. Effect of the noncompeting groundwater solutes Cl⁻, SO₄²⁻, HCO₃⁻, and HPO₄²⁻ at 5 mN using 2 g/L RNIP (48 wt% Fe⁰) at pH 8.9 (unbuffered), [TCE]ₒ = 0.027 mM. (a) Effect on TCE (in μmol) reduction. Lines represent the pseudo-first-order fit of the data. (b) Effect on H₂ evolution as %Fe⁰ in particles assuming 2.67 electron equivalents per mole of Fe⁰. Lines are not a fit of data and used only to guide the eye.

effect of HCO_3^- and PO_4^{3-} on the TCE degradation rate relative to SO_4^{2-} and Cl^- may also be from precipitation of Fe-carbonate (siderite−Fe(II)CO₃) and Fe-phosphate (vivianite−Fe(II)₃(PO₄)₂·8H₂O) onto the particle surface. Fe(II)-carbonate and -phosphate minerals are much less soluble than FeSO₄ and FeCl₂. The extent of precipitation cannot be extensive, however, because TCE degradation did not cease and there was no effect observed for H₂ evolution.

The final solution pH (9.5, 9.7, 9.9, and 10.2 for Cl^-, SO_4^{2-}, HCO_3^-, and HPO_4^{2-}, respectively) was slightly higher compared to pH 8.9 in the absence of solutes. The trend in the effect of anions on reactivity with TCE also correlates with the increasing trend in final pH so an effect of pH cannot be ruled out. However, RNIP reactivity with TCE has been shown to be a weak function of pH above ∼8 (*11*), and the TCE dechlorination rate with ZVI generally changes by less than a factor of 2 over one unit pH change (*1, 11, 35*), so factors other than pH should be responsible for the observed reduction of TCE reaction rate.

Groundwater ions can increase anodic corrosion by forming complexes with Fe^{2+} and, in some cases (HCO_3^- and HPO_4^-), may also increase cathodic corrosion by supplying H^+ which is reduced to H₂. Cl^-, SO_4^{2-}, HCO_3^-, and HPO_4^{2-}, however, had no significant effect on H₂ evolution at pH 9 over the 60 d period evaluated (Figure 3b). HCO_3^- appeared to slightly enhance Fe⁰ corrosion to form H₂ relative to DI and the other solutes, as has been reported (*19*); however this effect is small. The fact that H₂ evolution was unaffected by the solutes suggests that anion adsorption does not inhibit
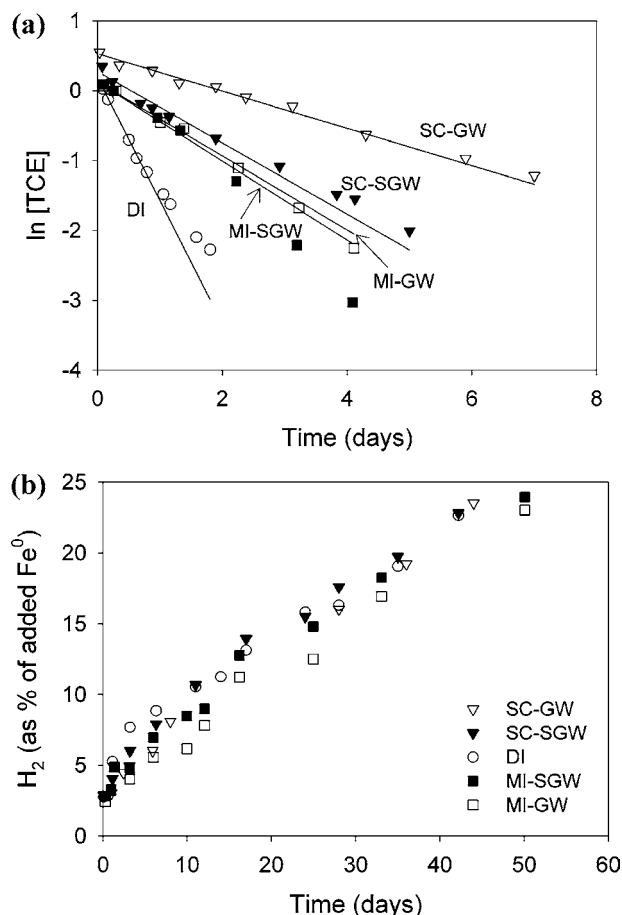
(a)

(b)

FIGURE 4. NZVI reactivity in groundwater from Parris Island, SC, and Mancelona, MI, and synthetic groundwater with an equivalent ionic composition but without organic carbon using 2 g/L RNIP (48 wt% Fe⁰), initial [TCE]ₒ = 0.027 mM. (a) TCE (in μmol) reduction. Lines are the pseudo-first-order fit of the data. (b) H₂ evolution as wt%Fe⁰ in particles assuming 2.67 electron equivalents per mole of Fe⁰. Lines are not a fit of data and used only to guide the eye.

the access of protons to the reactive sites. Solutes decreased the acetylene formation rate and TCE degradation rate similarly and therefore had little effect on the acetylene yield. This is consistent with the minimal effect on the H₂ evolution rate.

TCE Reduction and H₂ Evolution in Real Groundwater and Synthetic Groundwater. The groundwater from Mancelona, MI (MI-GW) and Parris Island, SC (SC-GW) contained commonly encountered anions (Cl^-, SO_4^{2-}, and HCO_3^-) and cations (Na^+, Ca^{2+}, and Mg^{2+}) (Supporting Information Table SI-1). MI-GW also contained 0.2 mM NO_3^- and had a low organic content (TOC = 0.76 mg/L) compared to SC-GW (TOC = 9.6 mg/L, NO_3^- was not detected). TCE reduction by NZVI in both SC-GW and MI-GW remained pseudo-first-order with respect to TCE, but the rate constants (k_{TCE}) for SC-GW and MI-GW were 7.4 and 3.5 times smaller than those in DI water, respectively (Figure 4). The k_{TCE} values measured in MI-GW and the synthetic groundwater (MI-SGW) with approximately the same inorganic composition (Supporting Information Table SI-1) were nearly the same (Table 1), indicating that the reduction in reactivity can be attributed to the presence of groundwater solutes. In contrast, k_{TCE} in SC-GW and in synthetic SC-SGW were different. k_{TCE} measured in SC-GW was 7.4 times smaller compared to that in DI but was only 3.4 times smaller compared to that in DI for SC-SGW (Table 1), indicating that inorganic solutes are only one of the factors affecting NZVI reactivity for SC-GW. The lower k_{TCE} in SC-GW compared to SC-SGW is attributed

to the high TOC content of SC-GW compared to MI-GW. Adsorbed organic matter on NZVI can block access of TCE to reactive sites and inhibit TCE dechlorination (*29, 36*). It should be noted that dissolved silica was shown to decrease the rate of arsenate and aresenite reduction by ZVI (*17*), so an effect of silica, which was not included in the synthetic groundwater, cannot be ruled out. The H_2 evolution rate in GW and SGW from both sites were not significantly different from that in DI water (Figure 4b).

Implications for Field Applications of NZVI. The simultaneous measurement of TCE loss and H_2 evolution provide insight into the surface reactions occurring. If all oxidants (H^+, TCE, NO_3^-) competed for a limited number of the same reactive sites, then increasing the concentration of one relative to the other should reflect this competition, and a similar effect of groundwater solutes on H_2 evolution and TCE reduction is expected. Several lines of evidence suggest that TCE and H^+ in fact do not compete for the same reactive sites under the conditions evaluated. First, the TCE concentration did not affect the rate of H_2 evolution, only the total produced at the end of the particle's lifetime. Second, groundwater solutes affected TCE reduction but not H_2 evolution. Third, $[NO_3^-] \leq 1$ mM slightly increased the rate of TCE reduction but slightly decreased the rate of H_2 evolution. If TCE and H^+ reduction indeed occur at different types of sites, there is potential for creating NZVI that is highly selective for TCE by increasing the number of TCE reactive sites and decreasing the number of H^+ reactive sites.

Because [TCE] does not significantly affect k_{TCE} (Figure 1), using NZVI for source zone treatment rather than for plume interception has several advantages. First, the TCE reduction rate increases proportionally with increasing TCE concentration ($k_{TCE} \times C_{TCE}$) and can provide rapid source zone mass reduction. Second, there are "less-reduced" reaction products (major acetylene with minor ethene and ethane) formed in the presence of DNAPL (i.e., higher TCE concentration). The reduction of TCE to acetylene requires fewer electrons (4 electrons/TCE) than to ethene (6 electrons/ TCE) or ethane (8 electrons/TCE). Therefore, more TCE can be dechlorinated in a source area per mass of NZVI compared to plume treatment. Third, less H_2 was produced at high TCE concentrations and thus more of the Fe^0 electrons are used directly to degrade TCE. It should be noted that evolved H_2 may eventually be used to degrade TCE via biodegradation, but the direct abiotic route will be the most efficient.

The NZVI reactive lifetime depends on the TCE concentration, and in the presence of TCE DNAPL, the reactive lifetime was <10 d. Thus, the reactive lifetime and the frequency of additional injection of NZVI, if required, will depend on the TCE concentration in the region where it is applied. The deviation of TCE reduction from the zero-order kinetics in the presence of DNAPL TCE implies that deactivation of the NZVI (passivation of iron surface) at TCE concentrations greater than 1.3 mM may be occurring. However, this deactivation does not limit the mass of TCE reduced per mass of NZVI added because all cases with different TCE concentrations appear to be converging on the same total Fe^0 consumption (Figure SI-2). Finally, the presence of commonly encountered groundwater anions at typical environmental conditions should not limit the applicability of NZVI or greatly affect its performance.

Acknowledgments

Supporting Information Available

NZVI-promoted TCE dechlorination pathways, method to convert the TCE reaction rate constant to the zero headspace condition, TCE dechlorination and the formation of acetylene, ethene, and ethane with time, and Fe^0 utilization with time. This material is available free of charge via the Internet at http://pubs.acs.org.

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